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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> :  B01D 71/02	A1	(11) International Publication Number: WO 90/15661  (43) International Publication Date: 27 December 1990 (27.12.90)
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(21) International Application Number: PCT/GB90/00945  
(22) International Filing Date: 19 June 1990 (19.06.90)  
(30) Priority data:  
8914023.0 19 June 1989 (19.06.89) GB

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(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE\*, DE (European patent)\*, DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.

Published

With international search report.

(54) Title: POROUS CERAMIC MEMBRANE AND METHOD

(57) Abstract

A free-standing ceramic membrane having pores of substantially uniform size can be formed by partly sintering a cast layer of ceramic particles including more than 60 % of larger particles and up to 40 % of smaller particles as a sintering aid. A composite membrane comprises as a support layer the free-standing ceramic membrane, and an overlying film of partly sintered ceramic particles. Both the support layer and the overlying films may be formed by tape casting dispersions of the particles in solutions of polymeric binder in preferably different volatile liquids.

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POROUS CERAMIC MEMBRANE AND METHOD

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This invention relates to porous ceramic membranes and methods of making them. Such membranes are increasingly being used as filters, as catalyst supports and in diagnostic applications, for they have the advantages of chemical inertness, good thermal resistance, high porosity and uniform pore size. The membranes are all characterised by having a particularly uniform pore size and narrow pore size distribution. In one aspect of this invention, the membrane is a composite membrane.

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Composite ceramic membranes, comprising a layer of partly sintered ceramic particles and an overlying film of partly sintered ceramic particles, are well known, and are described for example in EPA 242208 (Alcan International), GB 1605275 (CEA), US 20 4738874 (CEA), and Canadian 1196873 (Geceral). The overlying film is arranged to have narrower pores than the support layer. It is possible to make the overlying film very thin, with the result that the composite membrane combines good selectivity on the basis of particle size with high flux. Usually a dispersion of ceramic particles is applied to form a thin film on a pre-formed porous support layer. It is difficult to avoid penetration of the pores of the support by the dispersion, and this in turn makes it difficult to provide a uniform thin film of controlled thickness on the support layer. The problem is addressed in Canadian Patent 1196873, where a paste of ceramic particles comprising an organic polymeric binder is extruded as a tubular support layer, and then, while the pores are still full of the polymeric

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binder, a dispersion of ceramic particles is laid down as an overlying film, the support and the film being then heated in a single step to partly sinter the particles and form a composite structure.

5           US Patent 4652441 describes a technique of slurring ceramic particle agglomerates with binder and volatile solvent to form a slip, and tape-casting the slip on a smooth substrate at room temperature. A plurality of slip layers of the same composition and  
10 particle size may be cast to provide a laminated porous tape with enhanced strength.

Each of GB 1605248 and FR 2587026 and DE 3149796 describes the preparation of a porous body by heating a mass of refractory particulate material to  
15 partly sinter the particles, in which the refractory material is a mixture of particles of different sizes.

In one aspect, this invention provides a free-standing ceramic membrane having pores of substantially uniform size, formed by partly sintering  
20 a cast layer of ceramic particles consisting of 60 - 99% by weight of relatively larger particles and correspondingly from 40 - 1.0% of relatively smaller particles having an average diameter of from 4 nm up to 10% of the average diameter of the larger particles.  
25 The membrane may be made by providing a dispersion of ceramic particles in a solution of a polymeric binder in a volatile organic solvent, casting the dispersion to form a layer on a flat impervious surface, removing volatile solvent and heating the layer to partly sinter  
30 the particles.

In another aspect, this invention provides a composite porous ceramic membrane comprising a support layer which is a free-standing ceramic membrane as described, and an overlying film of partly sintered  
35 ceramic particles. These composite membranes may be made by various methods:-

i) The first method involves the use of a first dispersion of ceramic particles in a solution of a first polymeric binder in a volatile solvent, and of a second dispersion of ceramic particles in a volatile liquid which is a non-solvent for the first polymeric binder. The first dispersion is formed into a layer, preferably by tape-casting on a flat surface. Preferably after drying to remove volatile liquid but while the layer remains non-porous, the second dispersion is formed into a film of desired thickness overlying the layer. After removal of volatile materials, the composite is heated to partly sinter the ceramic particles and form the desired porous membrane.

Formulation of the first and second dispersions need to be performed in conjunction with one another. The granulometry of the first dispersion is preferably as described above.

ii) The second method involves providing a first dispersion of ceramic particles in a solution of a polymeric binder in a volatile solvent, and a second dispersion of ceramic particles in a volatile liquid which is a solvent for the polymeric binder, casting the first dispersion to form a layer, casting the second dispersion to form a film overlying the layer, removing the volatile solvent and heating to partly sinter the ceramic particles and form the desired porous membrane.

This method has the advantage over i) that selection of volatile liquids is not so critical. Provided that the overlying film is dried quickly, dissolution or disintegration of the support layer can be avoided. This may be achieved by casting the overlying film at high speed and at low film thickness. The granulometry of the first dispersion is preferably as described above.

iii) The third method involves providing a first dispersion of ceramic particles in a solution of a polymeric binder in a volatile solvent, providing a second dispersion of ceramic particles in a solution of a polymeric binder in a volatile solvent, casting the first dispersion to form a layer, separately casting the second dispersion to form a film, placing the film on the layer, and heating the layer and the overlying film to partly sinter the ceramic particles and form the desired composite porous membrane.

The granulometry of the first dispersion is preferably as described above. The preferably tape-cast layer and overlying films are laminated under pressure and mild heat (to soften the binder) to produce a flexible laminate which is cut or punched to size prior to sintering. This method has the advantages over i) and ii) that there are fewer limitations on the two formulations and on the casting conditions. It is possible to select a support layer and an overlying film to produce a range of pore sizes and chemistries.

According to a preferred feature of this invention, the ceramic particles in the first dispersion comprise 60 to 99%, preferably 80 to 95% by weight of relatively larger particles and correspondingly from 40 to 1.0%, preferably 20 to 5%, of relatively smaller particles. The larger particles may have an average size in the range 0.5 to 60 microns, particularly 1 to 20 microns, chosen to generate films with pores of desired size. The smaller particles may have an average size in the range 4 nm up to 2 micron, but not more than 0.1 times the average size of the larger particles. The smaller particles act as a sintering aid, permitting the layer to be sintered at lower temperatures than would otherwise be possible. It is generally preferable that the

relatively larger particles be of substantially uniform size, but the same is not true of the relatively smaller particles. The proportion of smaller particles should not be so great as to substantially block the pores between the larger particles.

5 In the case of a composite membrane, the smaller particles improve adhesion between the support and the overlying films. They also help to ensure that the composite membrane can be sintered in a single heating operation. If the smaller particles are absent, then the temperatures required to sinter the support layer and the overlying films may be so different that production of a porous composite membrane in a single heating step is impossible.

10 Alternatively, other kinds of sintering aids may be provided in the support layer, in an amount to approximate the sintering temperature of that layer to that of the overlying film. For example, a glassy material may be included in the first dispersion. Or the first dispersion may comprise a proportion of particles that soften at a relatively lower temperature than the remainder. For example, a proportion of silica particles may be included in a dispersion of zirconia and/or alumina particles. In this case, the relative sizes of the low-temperature-softening particles and of the remaining particles is not critical.

15 Tape-casting formulations, well known in the literature for firing to higher temperatures to produce dense non-porous membranes, are generally suitable. (See for example D.J. Shanefield and R.E. Mistler, Western Electrical Engineer, 15 (2) 26 to 31 (1971); and R.E. Mistler, Ceramic Bulletin, Volume 52, Number 11, 850 to 854 (1973)). The ceramic particles may be for example oxides, nitrides, borides or carbides, for example titania, alumina, ceria, zirconia, lead

zirconate titanate (PZT), silica, mullite, refractory metal oxides generally, and mixtures thereof.

5 The ceramic particles are preferably of a refractory metal oxide. When alumina is used, it may be useful to add a minor proportion of zirconia to increase the mechanical properties of the fired membrane. A preferred feature of the invention is that, when the ceramic particles are of zirconia, particles of alumina are also present in a minor  
10 proportion sufficient to increase the strength of the fired membrane.

The binder is a polymeric material with a molecular weight high enough to provide strength and toughness to the green tape. The binder preferably  
15 has a glass transition temperature below ambient, in order that the green tape may be sufficiently flexible to be bent or punched at ambient temperature. Alternatively, a plasticizer may be added to the tape casting formulation to improve flexibility. The binder  
20 should preferably be compatible with any dispersant used in the formulation, in order to avoid any possibility of phase separation. The binder should burn out cleanly during firing. Suitable polymeric binders include polyvinylbutyral, polyvinylalcohol,  
25 polyvinylpyrrolidone, polyacrylates and polymethacrylates including the methyl and higher esters, and cellulose and starch derivatives.

The binder is dissolved in a volatile solvent, which should preferably be inexpensive, non-  
30 toxic under the conditions of use, and have a vapour pressure sufficiently high that it is removed during drying without boiling. Suitable solvents are organic solvents such as trichloroethylene or methylethylketone or a mixture of one of them with ethanol.

35 The formulation may contain a dispersant to aid dispersion of the ceramic particles. Useful



dispersants include fish oil (predominantly derivatives of glyceryl trioleate) and corn oil. For use with fish oil, a preferred solvent is methylethylketone plus ethanol. For use with corn oil, a preferred solvent is trichloroethylene plus ethanol.

The porosity of the support layer, and if desired also of the overlying film, can be greatly increased by creating many isolated cavities within the membrane which are larger than the average pore size but not big enough to penetrate through to both surfaces of the membrane. Such cavities can be provided by incorporating in the formulation a pyrolysable particulate material which is coarser than the ceramic. These particles burn out during firing leaving cavities.

A suitable pyrolysable material is carbon. Hollow carbon spheres are especially suitable because they burn out without disrupting the surrounding ceramic particles. Hollow spheres 24 microns in diameter and with a wall thickness of 1.5 microns have been found to work well. The quantity of pyrolysable material that can be added is limited by the effect of the cavities on strength and the need to avoid creating so many cavities that they join up and penetrate through the thickness of the membrane.

These components are combined in a formulation of convenient application viscosity. In this the solvent concentration is preferably the minimum, or just slightly more than the minimum, required to make the viscosity suitable for casting. The binder concentration is sufficient to provide a green tape or membrane of adequate strength. An upper limit on binder concentration is set by the need to avoid "mud cracking" of the membrane during firing. Within these limits, it is surprisingly found that an increase in binder concentration tends to lead to an

increase in the overall porosity (though not to any significant extent the pore size) of the membrane after firing. It is therefore generally preferred to use a rather high binder concentration.

5           The formulation is cast in a uniform layer, thick enough to provide the desired strength both before and after firing, but thin enough to retain an adequate flux. Layers will typically be 0.01 to 2.0 mm thick after firing. Preferably casting is effected by  
10 the use of a doctor blade onto a flat impermeable substrate such as glass.

          If the formulation comprised a sintering aid as described above, and the cast layer is heated to remove volatile solvent and organic material and partly  
15 sinter the ceramic particles together, there results a ceramic membrane having good strength and freedom from warping. These membranes also have pores of substantially uniform pore size. For example, at least 75% of the pores are generally within 25% greater  
20 or less than the mean pore size. In preferred embodiments, at least 90% of the pores have a size within 10% of the mean. These figures are superior to those reported in the literature, and believed superior to those obtainable by using dispersions of particles  
25 of uniform size. In an alternative method of indicating pore size distribution, the membranes can be challenged with polystyrene beads. 100% retention of beads 20% larger than the average pore size (measured by mercury porosimetry) indicates a narrow pore size  
30 distribution in the case of sub-micron pores. It is possible that the uniform pore size is achieved because tape-casting the dispersion allows the particles to pack uniformly together.

          Instead of being used to make a free-standing  
35 ceramic membrane, the cast layer may be used as the support layer of a composite membrane. Method i) above

is the preferred method of making such a composite membrane. In this method, the second dispersion comprises ceramic particles in a volatile liquid which preferably also contains a polymeric binder. The ceramic particles may be chemically the same as or different from those in the first dispersion. The average size of particles in the second dispersion is generally chosen to be smaller than that of particles in the first dispersion, so that the overlying film has a smaller average pore size. As a rule of thumb, pore size after sintering is related to original particle size. Large particles, above about 1 micron in diameter result in a pore size of approximately 10% of the particle diameter. Sub-micron particles may tend to give a pore size which is about 50% of the particle diameter. The ceramic particles in the second dispersion preferably have an average particle size of from 0.1 to 50 microns.

The volatile liquid may conveniently be water. A water-soluble polymeric binder is preferably present, as this is found to reduce the tendency to cracking as the film is dried on the support layer. Suitable binders include cellulosic and vinyl derivatives and starches, methyl cellulose derivatives being particularly suitable. The formulation of the second dispersion needs to match that of the first dispersion, in particular so that:-

- a) Complete wetting of the layer occurs on application. This may be achieved by the use of a viscous second dispersion with a high content of ceramic particles. Viscosity also depends on other factors including particle size and agglomeration and organic binder content.
- b) No delamination of the film occurs on drying. This may be achieved by control over powder loading and polymer content of the second dispersion. Choice of

solvent and polymer should be such as to encourage shrinkage perpendicular to, rather than in, the plane of the film.

5 c) Shrinkage of the film matches that of the support layer on firing. Again, this is assisted by a high loading of ceramic particles in the second dispersion.

10 d) Partial sintering of both support layer and film occur at substantially the same temperature. In practice, this typically requires adjustment of the constituents of the support membrane to match the sintering temperature of the applied layer.

The second dispersion is cast, preferably by tape-casting using a doctor blade as before, on to the support layer. This support layer has preferably been dried before receiving the second dispersion, although this is not absolutely necessary particularly where some intermingling of the two is acceptable. The volatile liquid of the second dispersion is a non-solvent for the polymeric binder of the first layer, and as a result there is no significant migration of the first polymeric binder from the layer into the film. Because the support layer is flat and non-porous, it is easy to cast the second dispersion as a smooth coating of uniform thickness on it, without any interpenetration of the two. The film needs to be continuous, i.e. a complete skin, but thin enough to provide an adequate flux.

30 Casting by doctor blade can be used to form a flexible uniform tape of substantial area. Using another doctor blade, it is easy to cast the second dispersion over the entire surface of the first one. The resulting simple or composite membrane is then dried until it becomes self-supporting and removed from its support. The green membrane is flexible and can be formed into spirals, tubes or corrugated membranes,

which is useful for increasing the specific surface area of a filter. Surprisingly, the membrane in the green state can be embossed and retain its embossed pattern after firing. It is possible to emboss channels for liquid flow in filters or diagnostic devices.

The green membrane is then heated to a temperature in the range 600 to 1600°C sufficient to burn off organic material and partly sinter the ceramic particles together. During heating, a stack of pieces of the composite membrane may be subjected to pressure to reduce buckling. It is an advantage of the invention that both layer and film are fired at the same time, so that only a single heating step is required.

In the resulting fired membrane:-

- i) The pore size is determined essentially by the size of the particles used to form the overlying film.
- ii) The porosity (or flux) is determined by several factors, including ceramic particle size of support layer and film; thickness of support layer and film; the amount of binder used in formulating the support layer and overlying film; and the possible presence of pyrolysable particles, e.g. hollow carbon spheres, in the formulation for the support layer.

The following examples illustrate the invention.

#### EXAMPLE 1

Fabrication of a single layer ceramic membrane by tape casting.

150g of alumina (1.5 µm particle size) and 12.2g zirconia (240Å crystallite size) were slurried in a liquid system composed of 82g trichloroethylene, 33g ethanol, 4.2g corn oil, 12g polyvinyl butyral and 16g polyethyleneglycol. The ball milled slurry was

tape cast on a glass substrate into a film of width 173mm, which was dried to yield a flexible tape of thickness 0.17mm. Discs of diameter 26.5mm were cut from the tape and partially sintered at 1475°C for 1 hour, to produce a 25mm diameter ceramic membrane with a porosity of 53% and an average pore size of 0.48  $\mu\text{m}$ . The pore size distribution of the membrane was surprisingly sharp with >80% of the pores within  $\pm 10\%$  of the average diameter. When an aqueous suspension of 0.5  $\mu\text{m}$  polystyrene beads was filtered through the membrane it retained 100% of the beads. The permeability of the membrane to pure water was 19 ml/minute/cm<sup>2</sup> at 70 kPa. The chemical resistance of the membrane was excellent. No weight loss was experienced when the porous ceramic discs were immersed in pH 1 (buffer HCl) and pH 10 (alkaline phosphatase) solution for 100 hours at 20°C.

#### EXAMPLE 2

Fabrication of a double layer membrane by tape casting  
70g of coarse zirconia (14  $\mu\text{m}$  particle size), and 7g of fine zirconia (240Å<sup>0</sup> crystallite size), 3.5g yttria and 9g (1.5  $\mu\text{m}$  particle size) alumina were slurried in a liquid system composed of 2.5g Menhaden fish oil, 22g methyl ethyl ketone, 13g ethanol, 7g polyvinylbutyral and 9g poly-ethyleneglycol. The slurry was tape cast on a glass substrate into a film of width 173 mm, which was dried in air to yield a flexible tape of thickness 0.31 mm. A second slurry composed of 25g of zirconia (2.5  $\mu\text{m}$  particle size) and 1.25g yttria was dispersed in a solution of 3.5g methocel polymer in 100 ml water, and then cast as a thin layer on top of the first tape and allowed to dry at RT. The double layer green tape was punched into discs of diameter 27 mm and partially sintered at 1475°C to produce a porous composite membrane 24 mm in

diameter. The pore diameter of the support and top coat were 1.4  $\mu\text{m}$  and 0.42  $\mu\text{m}$  respectively. The permeability of the composite membrane to pure water was 35 ml/min/cm<sup>2</sup> at 70 kPa. The membrane gave a 100% retention of 0.5  $\mu\text{m}$  polystyrene beads when an aqueous suspension of the beads were filtered through. The chemical resistance of the membrane was good. No weight loss was experienced in pH 1 and pH 10 solutions over a 100 hour immersion period.

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EXAMPLE 3

a). 70 g of zirconia with an average particle size of 1  $\mu\text{m}$ , 14 g of zirconia with a crystallite size of 240 Angstroms and 3.5 g yttria were slurried in a liquid system composed of 23 g methylethylketone, 11 g ethanol, 4 g fish oil, 5 g polyvinylbutyral and 3 g polyethyleneglycol. The slurry was cast into a tape, cut into discs and fired at 1500°C for 1 hour. The partially sintered ceramic had poor mechanical strength and could not be used as a membrane filter in a stirred cell.

b) When 9 g of alumina (particle size 1.5  $\mu\text{m}$ ) was added to the slurry described in Example 1 and processed in a similar manner, there was a significant improvement in the mechanical strength of the resultant ceramic; it was suitable for use as a filter in a stirred cell.

Average pore size was 0.48  $\mu\text{m}$   
Porosity was 38.5%  
Flow rate 0.86ml/min/cm<sup>2</sup> at 70 kPa on a membrane 340  $\mu\text{m}$  thick.

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EXAMPLE 4

To the formulation of Example 3b was added 3 g of hollow carbon spheres, 21  $\mu\text{m}$  average diameter and 1.5  $\mu\text{m}$  wall thickness supplied by Versar Manufacturing Inc, Virginia. The slurry was cast and fired as in Example 3.

The resulting membrane had an average flow rate of 3.5ml/min/cm<sup>2</sup> at 70 kPa on a membrane 320  $\mu\text{m}$  thick.

Examination of the membrane in the SEM revealed the presence of large discrete spherical voids within the membrane, which contributed to an increased porosity without increasing the effective pore size of the filter.

EXAMPLE 5Preparation of a support layer by tape casting

140 g of coarse unstabilised zirconia (14  $\mu\text{m}$  particle size), 4 g of fine stabilised zirconia (240  $\text{\AA}$  crystallite size), 7 g yttria (sub micron particle size) and 15 g alumina (1.5  $\mu\text{m}$  particle size) were slurried in a liquid system composed of 0.5 g Mazola (Trade Mark) corn oil, 40 g trichloroethylene and 16g anhydrous ethanol. The slurry was ball milled for 3 hours. 8 g polyvinylbutyral and 9 g polyethyleneglycol were added to this slurry which was then ball milled for a further 18 hours. The resultant slurry was tape cast on to a clean glass substrate into a film of width 173 mm which was dried in air to yield a flexible tape. A doctor blade height of 850  $\mu\text{m}$  resulted in a green tape that was 350  $\mu\text{m}$  thick.

A microporous top layer was then applied on this support layer by one of three methods.



EXAMPLE 6Casting on the support layer using a different (aqueous) solvent

An aqueous slurry composed of 35 g of zirconia (2.5  $\mu\text{m}$  particle size) and 2.1 g yttria dispersed in a solution of 0.1 g of Darvan C surfactant (an ammonium salt of a polyelectrolyte from R. T. Vanderbilt Co., CT, USA) in 25 ml of water, was ball milled for 17 hours. 80 ml of a 5% solution of Methocel polymer (Dow Chemicals) was then added and the resultant slurry ball milled again for a further 1 hour. This slurry was then cast as a thin layer on top of the support tape and allowed to dry at room temperature. A blade height of 425  $\mu\text{m}$  (of which a height of 350  $\mu\text{m}$  is to allow for the thickness of the base layer) resulted in a top coat that was about 75  $\mu\text{m}$  thick. The double layer green tape was punched into discs of diameter 26 mm and partially sintered at 1475°C to produce a porous composite membrane which was 400  $\mu\text{m}$  thick and 25 mm in diameter. The pore diameters of the support and top coat were 3.6  $\mu\text{m}$  and 0.40  $\mu\text{m}$  respectively. The permeability of the composite membrane to pure water was 30 ml/min/cm<sup>2</sup> at 70 kPa. The membrane gave a 100% retention of 0.45  $\mu\text{m}$  polystyrene beads when an aqueous suspension of beads were filtered through the membrane.

EXAMPLE 7Casting on the support using organic solvents

133 g of monoclinic zirconia (less than 10  $\mu\text{m}$  particle size) and 17.2 g of alumina (1.5  $\mu\text{m}$  particle size) were slurried in a solution of 1.4 g Menhaden fish oil dispersant in 11 g methyl ethyl ketone and 11g anhydrous ethanol. The slurry was ball milled for 3 hours. 19 g of a polymer (Paraloid from Rohm and Haas Co.), 3.4 g polyethyleneglycol (molecular weight

400), 4.4 g butylbenzylphthalate and 0.8 g cyclohexane were then added and the resultant slurry was ball milled for a further 2 hours. This organic solvent based slurry was then tape cast on the support layer.

5 There was no dissolution of the support layer polymer or disintegration of the base if the top coating dried into a film as quickly as possible. This was achieved by increasing casting speed and reducing coating thickness. The double layer tape was punched into

10 discs and sintered at 1475°C to produce composite membranes.

#### EXAMPLE 8

##### Laminating a second tape onto the support tape

15 The second tape was prepared by casting a slurry composed of 70 g zirconia (2.4 µm particle size), 7 g fine zirconia (240 Å crystallite size), 3.5 g yttria (submicron particle size) and 9 g alumina (1.5 µm particle size) in 28 g methylethylketone, 17 g

20 ethanol, 6 g Menhaden fish oil, 9 g polyvinylbutyral and 13 g polyethyleneglycol. The ball milled slurry was cast using a blade height of 50 µm, dried in air and then stripped from the glass substrate. The tape was then placed on top of the support tape and pressed

25 together at a pressure of 5 bar for a period of 2 minutes between heated metal plates maintained at 80°C. The laminated tape was then punched and fired to produce a composite porous ceramic membrane. The support layer was 180 µm thick and had an average pore

30 size of 3.5 µm whilst the separation layer was 10 µm thick and had an average pore size of 0.40 µm. The pore size distribution of the separation layer was narrow with 85% of the pores within ±25% of the average diameter.

CLAIMS

- 5
1. A free-standing ceramic membrane having pores of substantially uniform size, formed by partly sintering a cast layer of ceramic particles consisting of 60 - 99% by weight of relatively larger particles and correspondingly from 40 - 1.0% of relatively smaller particles having an average diameter of from 4 nm up to 10% of the average diameter of the larger particles.
- 10
2. A membrane as claimed in Claim 1, wherein the smaller particles constitute from 5 - 20% by weight of the ceramic particles.
- 15
3. A membrane as claimed in Claim 1 or Claim 2, wherein the larger particles are of substantially uniform size.
- 20
4. A composite porous ceramic membrane comprising a support layer which is a free-standing ceramic membrane according to any one of Claims 1 to 3, and an overlying film of partly sintered ceramic particles.
- 25
5. A composite membrane as claimed in Claim 4, wherein the overlying film has a smaller average pore size than the support layer.
- 30
6. A membrane as claimed in any one of Claims 1 to 5, wherein the ceramic particles are of a refractory metal oxide.
- 35
7. A membrane as claimed in Claim 6, wherein the ceramic particles are of zirconia.
8. A membrane as claimed in Claim 7, wherein particles of alumina are also present in a minor proportion sufficient to increase the strength of the fired membrane.

9. A method of making the membrane of any one of Claims 1 to 3, which method comprises providing a dispersion of ceramic particles in a solution of a polymeric binder in a volatile organic solvent, casting  
5 the dispersion to form a layer on a flat impervious surface, removing volatile solvent and heating the layer to partly sinter the particles.

10. A method of making a composite porous ceramic membrane which method comprises providing a first  
10 dispersion of ceramic particles in a solution of a polymeric binder in a volatile solvent, and a second dispersion of ceramic particles in a volatile liquid which is a non-solvent for the polymeric binder, casting the first dispersion to form a layer, casting  
15 the second dispersion to form a film overlying the layer, removing volatile materials and heating to partly sinter the ceramic particles and form the desired porous membrane.

11. A method as claimed in Claim 10, wherein the  
20 layer cast from the first dispersion is dried before the second dispersion is cast on it.

12. A method as claimed in Claim 10 or Claim 11, wherein the second dispersion comprises a polymeric binder in solution in the volatile liquid.

25 13. A method as claimed in any one of Claims 10 to 12, wherein the volatile solvent of the first dispersion is organic and the volatile liquid of the second dispersion is aqueous.

14. A method of making a composite porous ceramic  
30 membrane which method comprises providing a first dispersion of ceramic particles in a solution of a polymeric binder in a volatile solvent, providing a second dispersion of ceramic particles in a solution of a polymeric binder in a volatile solvent, casting the  
35 first dispersion to form a layer, separately casting the second dispersion to form a film, placing the film

on the layer, and heating the layer and the overlying film to partly sinter the ceramic particles and form the desired composite porous membrane.

15. A method of making a composite porous ceramic membrane, which method comprises providing a first dispersion of ceramic particles in a solution of a polymeric binder in a volatile solvent, and a second dispersion of ceramic particles in a volatile liquid which is a solvent for the polymeric binder, casting the first dispersion to form a layer, casting the second dispersion to form a film overlying the layer, removing the volatile solvent and heating to partly sinter the ceramic particles and form the desired porous membrane.

16. A method as claimed in any one of Claims 9 to 15, wherein casting is effected by tape casting.

17. A method as claimed in any one of Claims 10 to 16, wherein the first dispersion of ceramic particles includes a sintering aid in an amount to approximate the sintering temperature of the layer to that of the overlying film.

18. A method as claimed in any one of Claims 10 to 17, wherein the first dispersion of ceramic particles consists of 60 - 90% by weight of relatively larger particles and correspondingly from 40 - 1.0% of relatively smaller particles having an average diameter of from 4 nm up to 10% of the average diameter of the larger particles.

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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 90/00945

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> : B 01 D 71/02		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System <sup>1</sup>	Classification Symbols	
IPC <sup>5</sup>	B 01 D 71/00	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	FR, A, 2587026 (CNRS) 13 March 1987 see the whole document see claim 10 (cited in the application)	1   4
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A	DE, A, 3149796 (ELEKTROSCHMELZWERK KEMPTEN GmbH) 23 June 1983 see the whole document (cited in the application)	1
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A	GB, A, 1605248 (THE MOND NICKEL CO.) 5 March 1986 (cited in the application)	
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./.		
<p><sup>10</sup> Special categories of cited documents: <sup>14</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14th September 1990	11. 10. 90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	F.W. HECK <i>Heck</i>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	FR, A, 2502508 (GECERAL) 1 October 1982 see claim 6  -----	10,15

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9000945  
SA 37563

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 02/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2587026	13-03-87	EP-A, B 0219383	22-04-87
DE-A- 3149796	23-06-83	None	
GB-A- 1605248	05-03-86	CA-A- 1198004	17-12-85
FR-A- 2502508	01-10-82	CA-A- 1196873	19-11-85
		JP-A- 58034006	28-02-83